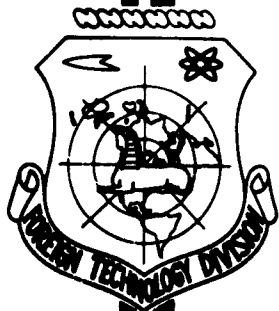63-3-2

TRANSLATION

KINETICS OF THE DARK REACTION OF THE CHLORINE-
HYDROGEN MIXTURE, III AND IV

By

A. I. Rozlovskiy

FOREIGN TECHNOLOGY
DIVISION

AIR FORCE SYSTEMS COMMAND

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UNEDITED ROUGH DRAFT TRANSLATION

KINETICS OF THE DARK REACTION OF THE CHLORINE-HYDROGEN
MIXTURE, III AND IV

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KINETICS OF THE DARK REACTION OF THE CHLORINE-HYDROGEN MIXTURE

III. NORMAL COMBUSTION OF CHLORINE-HYDROGEN MIXTURES

A.I. Rozlovskiy

In earlier installments [1, 2], we formulated the basic kinetic qualitative laws governing the thermal (dark) reaction between chlorine and hydrogen at low temperatures. The singularities of the reaction mechanism and the conditions for self-ignition of chlorine-hydrogen mixtures that were analyzed in the above reports necessitated studying the kinetics of the reaction in the flame and served as a point of departure for such an investigation, which is interesting in several respects.

On the one hand, its combination with the results of study of the pre-flame reaction gives detailed information concerning the kinetics of this important reaction in a broad range of temperature variation. On the other hand, the model reaction of a hydrogen-chlorine mixture having a well-studied (at low temperatures) mechanism is a suitable object for verification of the qualitative laws of normal-combustion theory, and, in particular, for determining the absolute values of the reaction rate in the flame. Finally, study of the combustion of H_2 + Cl_2 mixtures should assist in determining the unknown mechanism of homogeneous initiation of the active centers for this reaction, which is of fundamental importance for the theory of the thermal explosion.

The comparative simplicity and stability of the kinetics of the chlorine-hydrogen reaction render the present investigation central to a number of the author's studies [3-5], which were devoted to verifi-

cation and substantiation of the normal-combustion theory of Ya.B.
Zel'dovich and D.A. Frank-Kamenetskiy.

EXPERIMENTAL TECHNIQUE

Thermodynamic Calculations for State of Combustion Products

Flame speeds in chlorine-hydrogen mixtures were measured at initial pressures from 35 to 260 mm Hg in a round glass flask 100 mm in diameter, with central ignition. The flame was photographed on a rotating film using the usual technique; the photographs were made without the slit [6]. Ignition of the mixture was synchronized with closing of the lens on the photographic recording apparatus to cut off the glow from the combustion products.

The mixtures investigated were prepared and stored in mixers. The components were proportioned on the basis of their partial pressures, with subsequent analysis of the mixture for its chlorine content. The pressure was measured with a mercury manometer; the surface of the mercury was protected from attack by the chlorine by a layer of vaseline oil.

The technique of experimentation with chlorine-hydrogen mixtures was further complicated by the action of chlorine on the stopcock lubricants and on the rubber connecting tubes. To prevent the photochemical reaction, the work was done in red light. The mixers were enclosed in an opaque shell and the connecting tubes were painted black. The outside surfaces of all valves in the apparatus were painted in the same way, since, according to Morris and Pease [7], the reaction of chlorine with the vacuum lubricant is photochemical.

(Electrolytic) hydrogen was taken from the technical-grade cylinder and dried by freezing out the water vapor (from the gas holder) with liquid air. The chlorine was obtained by reacting hydrochloric acid with $KMnO_4$ with subsequent purification by washing with water (elimi-

nation of hydrogen chloride), freezing with liquid air and fractionation. The hydrogen chloride was obtained by dropwise addition of concentrated hydrochloric acid to concentrated sulfuric acid; it was purified by freezing out with liquid air and fractionation.

To determine the chlorine content, a sample of the gas was withdrawn into a dry evacuated gas pipette with a capacity of about 150 cm^3. After the sample had been taken, 20-30 cm^3 of a 10% solution of potassium iodide was sprinkled into the pipette; the iodine that was liberated was titrated with hyposulfite.

The experiments indicated that the flame is intensely luminous (in the visible region) only in chlorine-rich mixtures. The luminosity of mixtures leaner than stoichiometric drops off rapidly with diminishing chlorine content. The flame of a mixture containing less than 30% of chlorine can no longer be photographed on the most sensitive of the films that we used (GOST 250), in spite of the fast optical train ("Yupiter" lens with $D = 1:1.5$) and exposure without the slit, which gives the highest possible illumination of the negative.

As we know, direct measurement gives only the quantity u_b — the speed of the flame with respect to the fixed combustion products — in spherical flame propagation. To convert u_b to u_n — the normal speed of the flame — it is necessary to determine the ratio of the densities of the gaseous mixture before (ρ_0) and after (ρ_b) combustion: $\mu = \rho_0/\rho_b$, since it follows from the condition of conservation of matter that

$$u_n\rho_0 = u_b\rho_b.$$

It is further necessary to find the temperature of combustion T_b, which is the basic characteristic of the reaction in the flame. The quantities T_b and μ were determined by thermodynamic calculation, which was performed by the method of Ya.B. Zel'dovich and A.I. Polyarnyy

[8] after certain modifications by the author.

Let $\underline{p}$ denote the total pressure of the mixture, and let the partial pressures of the components be denoted by their chemical symbols. For the equilibrium equations that we have selected

$$H_2 / \sqrt{H_2} = K_{34},$$
$$Cl_2 / \sqrt{Cl_2} = K_{34},$$
$$\sqrt{H_2 \cdot Cl_2} / HCl = K_{34},$$

the values of the equilibrium constants have been tabulated [8].

In view of the simplicity of the H—Cl system, it is more convenient to reduce the mass-balance equations to the form proposed by A.P. Vanichev [9]. Let γ denote the total proportion of chlorine in the mixture (free and bound), and let Cl_2^O, H_2^O and HCl^O be the partial pressures of the components of the original mixture; then

$$\gamma = \frac{Cl_2^O + 0.5\,HCl^O}{p}.$$

Denoting the number of gram atoms of H and Cl in the mixture by $[H]_0$ and $[Cl]_0$, we write

$$\frac{[Cl]_0}{[H]_0} = \frac{\gamma}{1-\gamma} = \frac{2Cl_2 + Cl + HCl}{2H_2 + H + HCl}.$$

It follows from the condition of combustion at constant pressure that

$$Cl_2 + Cl + H_2 + H + HCl = p.$$

With this notation for the mass-balance equations, there is no need to interpolate the enthalpy of the combustion-product mixture over pressure, as is necessary in the Zel'dovich-Polyarnyy method.

The equation of energy conservation takes the form

$$\sum p_j^0 H_j^{T_0} = \sum p_i^T H_i^{T_0},$$

where p_j^0 and p_i are the partial pressures of the initial components and the combustion products at the corresponding temperatures; $H_j^T 0$ and $H_i^T b$

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are the corresponding enthalpies, and T_0 is the temperature of the starting mixture.

Fig. 1. Combustion temperature of $H_2 + Cl_2$ mixtures as a function of composition. 1) 0.1 atm abs; 2) 0.2 atm abs; 3) 0.4 atm abs.
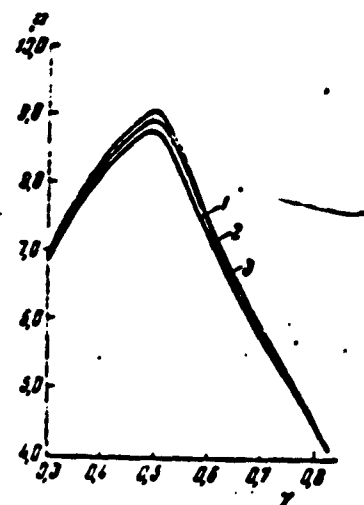
Fig. 2. Density change of $H_2 + Cl_2$ mixtures on combustion as a function of composition: 1) 0.1 atm abs; 2) 0.2 atm abs; 3) 0.4 atm abs.

In the calculations, we used the system of reckoning the enthalpies from an arbitrary zero which is similar to that used by Ya. B. Zel'dovich and A.I. Polyarnyy; the enthalpy of gaseous chlorine at the absolute zero of temperature was taken as the null. The enthalpies for H and H_2 were taken from the tables [8], while the enthalpies of Cl, Cl_2 and HCl were computed by the author from the elementary thermodynamic formulas, without taking the anharmonicity of the atomic oscillations in the molecules into account. Here, the following fundamental oscillation frequencies were assumed for the atoms in the molecule: 565 cm^{-1} for Cl_2 and 2989 cm^{-1} for HCl [10]. The dissociation heat of Cl_2 into the atoms was set equal to $\Delta H^{T=0} = 2 \cdot 28.45$ kcal/mole [11], and the heat effect of formation of hydrogen chloride from the elements was assumed equal to 22.06 kcal/mole at 291° K [12].

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The calculations indicate that the combustion temperatures of hydrogen-chlorine mixtures are relatively low. In chlorine-rich mixtures, the equilibrium concentrations of H_2 and H are so small even for $\gamma = 0.6$ (in binary $H_2 + Cl_2$ mixtures) that their total heat capacity does not exceed [illegible] % of the combustion-product enthalpy; if the quantities H_2 and H are disregarded, the calculation technique is simplified.

The quantity μ is found from the relationship

$$\mu = \frac{T_b}{T_0} \eta(T_b).$$

where η is the change in the number of molecules during the reaction:

$$\eta = \frac{H + Cl}{2p} + 1.$$

On the basis of the calculated data for the equilibrium composition, we plot a graph of η as a function of temperature and use it to determine $\eta(T_b)$ for a certain value of T_b. Certain results of the state calculations for the combustion products of mixtures with $HCl^0 = 0$ are given in Figs. 1 and 2.

In investigating the reaction kinetics in the flame, we diluted the combustible mixture with reaction products and replaced part of the excess component with hydrogen chloride. Here only the quantity $\Sigma p_j^0 H_j^0$ changes. Fig. 3 shows the combustion temperature as a function of the content α (mole fraction) of the combustion-product additive for mixtures with $\gamma = 0.4$, 0.5, 0.6 and 0.7 at $p = 0.2$ atm abs; Fig. 4 shows similar diagrams for the quantity μ. For intermediate γ, the values of the corrections $T_b(\alpha)$ and $\mu(\alpha)$ were found by graphical interpolation.

In studying the influence of the excess-component content on the speed of the flame, constancy of the deficient-component contents [6]
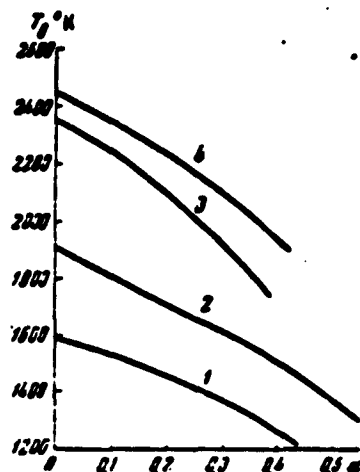
Fig. 3. Combustion temperature as a function of content of combustion-product additive (p = 0.2 atm abs): 1) γ = 0.7; 2) γ = 0.6; 3) γ = 0.4; 4) γ = 0.5.
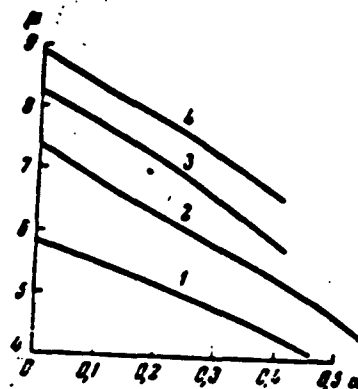
Fig. 4. Change in mixture density on combustion as a function of content of combustion-product additive (p = 0.2 atm abs): 1) γ = 0.7; 2) γ = 0.6; 3) γ = 0.4; 4) γ = 0.5.

no longer insures constancy of combustion temperature, since the components of such mixtures are not thermodynamically equivalent. Replacement of one of the components by hydrogen chloride changes not only the quantity $\Sigma p_j^0 H_j^0$, but also γ. Letting $\underline{a}$ denote the mole fraction of hydrogen in the mixture and β that of hydrogen, we write

$$\gamma = 1 - a - \beta/2.$$

The combustion temperatures are determined for values of β corresponding to the γ for which the equilibrium-composition calculation has been made; the T_b are computed by the usual graphic method. The values of T_b for given β are found by graphic interpolation.

Combustion of Binary H_2 + Cl_2 Mixtures

Flame speed was investigated as a function of pressure for five binary mixtures containing 50.0, 72.0, 76.2, 79.7 and 82.3% of Cl_2 in the pressure range from 36 to 260 mm Hg. The normal speeds of the flame

were computed using the given thermodynamic calculations.

The results of study of normal flame speed as a function of pressure are given in logarithmic coordinates in Fig. 5. In spite of a certain scattering of the points, it is obvious from the diagram that for the four mixtures investigated in detail, the normal speed of flame propagation may be regarded as virtually independent of pressure; only in the mixture that was richest in chlorine, with $\gamma = 0.823$, do we note a drop of U_n with rising pressure.
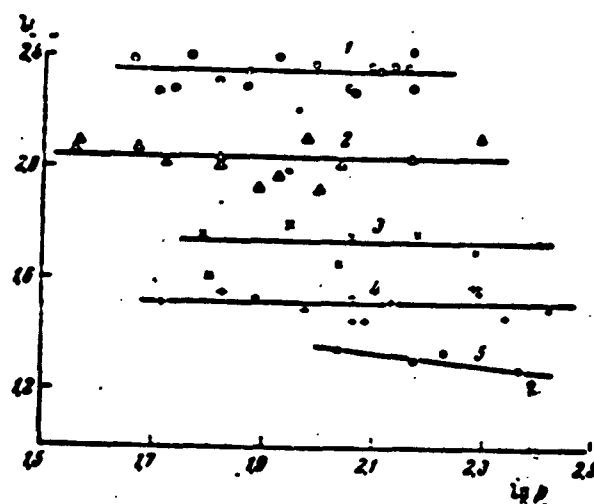
Fig. 5. Normal rate of flame propagation as a function of pressure: 1) $\gamma = 0.500$; 2) $\gamma = 0.720$; 3) $\gamma = 0.762$; 4) $\gamma = 0.797$; 5) $\gamma = 0.823$.

Since the dependence of μ on pressure is only weakly expressed, we may assume in approximation that not only u_n but u_b as well are independent of pressure. Extending this property of Cl_2-H_2 mixtures to all of the compositions studied, we shall henceforth assume that the results of all experiments are referred to a standard pressure of 0.2 atm abs.

The dependence of flame velocity on composition was also studied for binary mixtures. Here, the mixtures investigated were prepared in the explosion vessel itself by alternating admission of appropriate

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TABLE 1

γ	1 u_B cm/sec	2 u_R cm/sec	3 u_B/u_R
0.500	350	224	1.56
0.445	405	221	1.83
0.355	360	208	1.73

1) u_B, cm/sec; 2) u_R, cm/sec; 3) u_B/u_R.

portions of the two basic mixtures, which were available in mixers. The experimental results appear in Fig. 6 in the coordinates log $u_n : \gamma$; the diagram also indicates the averaged values of u_n for the series of experiments described above; these values are keyed by other symbols. It follows from the diagram that the speed of the flame reaches its maximum near the stoichiometric composition and is unsymmetrical for excesses of chlorine and hydrogen.

In connection with these last results, we should take note of the data obtained by Bartholome [13], who measured several values of u_n for chlorine-hydrogen mixtures in a Bunsen flame at atmospheric pressure. The data of Bartholome (u_B) and the author (u_R) are assembled in Table 1; the comparison is naturally valid if u_n = const right up to p = 1 atm abs.
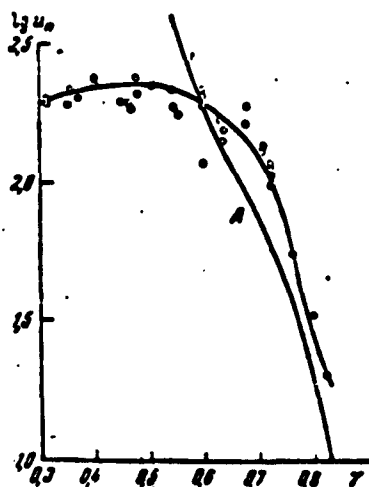

Fig. 6. Normal speed of flame in binary mixtures of H_2 + Cl_2 as a function of composition. Curve A will be described in a subsequent report.

The values of u_n found by Bartholome are noticeably larger than ours and correspond to a position of the flame-speed maximum at $\gamma < 0.5$. It is not yet possible to account for this divergence. We note only that if u_n is measured with error in a spherical flame, we should expect the values to be high rather than low with any distortion of the flame sphere.

Influence of Reaction-Product Additives and Content of Excess Component on Speed of Flame

The technique that we used — that of diluting the test mixture with its re-

action products with the objective of determining the activation energy of the reaction in the flame – was proposed by P.Ya. Sadovnikov and was first employed by G.A. Barskiy and Ya.B. Zel'dovich [6] in a study of combustion of carbon-monoxide mixtures.

TABLE 2

$-\dfrac{\gamma}{\dfrac{d \lg u_n}{d(10^3/T_b)}}$	0.596	0.500	0.598	0.720
	0.60	2.24	3.82	3.50
1) A', $\dfrac{kcal}{mole}$	60.4	20.5	35.0	32.6

1) A', kcal/mole.

In our experiments, the mixtures to be investigated were prepared in the explosion vessel itself. For this purpose, a certain quantity of the combustion products from the preceding experiment was left in the reactor in preparing for each new experiment. The upper limit of the additive concentration (from 32 to 50%) is imposed by a sharp drop in the actinicity of the flame or by failure of combustion. Here, the investigated combustion-temperature range extends from 376° for the mixture $\gamma = 0.720$ to 500° for the mixture with $\gamma = 0.598$.

The author studied mixtures with $\gamma = 0.396$, 0.500, 0.596 and 0.720. The results of the experiments are presented in Fig. 7 in the coordinates log u_n: $1/T_b$, from which it follows that the points for all four mixtures fit straight lines satisfactorily over the entire combustion-temperature interval studied. The effective values of the flame-speed temperature coefficient may be computed from the slope of these lines, as well as the apparent activation-energy values A'.

We may assume in first approximation that the rate of the reaction in the flame

$$\omega \sim e^{-A'/RT_b},$$

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where A' is the apparent energy of activation; then, according to [14]

$$u_n \sim e^{-A'/2RT_b}.$$

The results of the calculations are presented in Table 2.

As will be seen from Table 2, the temperature coefficients of flame speed are practically the same in both excess-chlorine mixtures and correspond to a value of A' close to the activation energy of the pre-flame reaction, i.e., 35 kcal/mole. The value of A' for the stoichiometric mixture is considerably lower than this figure. It must be assumed that this deviation is an effect of the profound dissociation of the reaction products similar to that observed in studies of the combustion of NO + H_2 mixtures [4, 5]. The considerable increase in activation energy for the mixture with the hydrogen excess is apparently related to the essentially different mechanism by which active centers form in these mixtures.
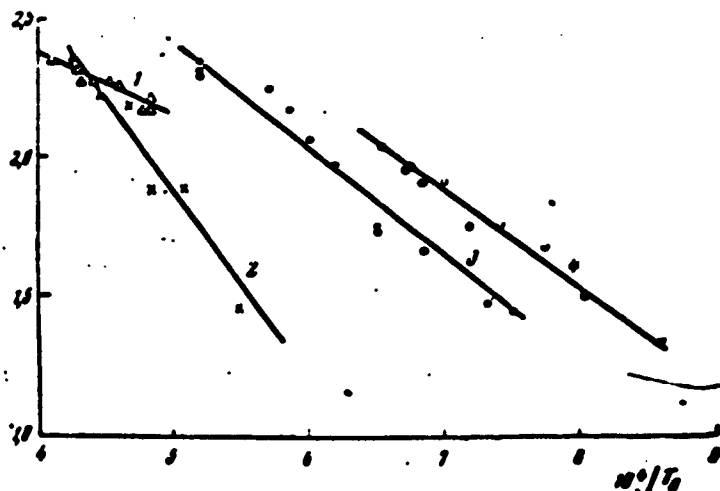

Fig. 7. Determination of apparent temperature coefficient of reaction speed in flame:
1) γ = 0.500; 2) γ = 0.396; 3) γ = 0.598;
4) γ = 0.720.

Using the example furnished by combustion of a CO + O_2 + N_2 mixture, Reference [6] describes a method for studying the kinetics of the flame reaction by varying the concentration of the excess component
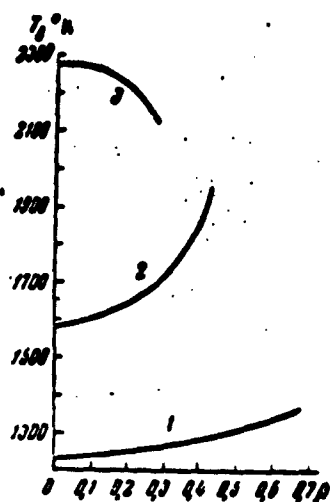
Fig. 8. Variation of
combustion temperature
on partial replacement
of the excess compon-
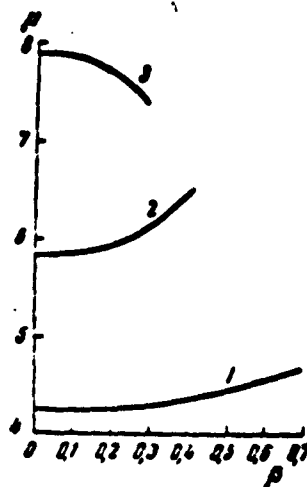ent by hydrogen chlo-
ride: 1) a = 0.177; 2)
a = 0.294; 3) b = 0.369.

Fig. 9. Influence of
partial replacement of
excess component by
hydrogen chloride on
density of mixture
during combustion: 1)
a = 0.177; 2) a = 0.294;
3) b = 0.369.

while holding other parameters constant, in this case with partial re-
placement of the excess O_2 or CO by an inert diluent — nitrogen. The
author undertook an attempt to make an analogous study of the influence
of the excess-component concentration for chlorine-hydrogen mixtures.
Hydrogen chloride was selected as the inert diluent.

However, the physical pattern of combustion in chlorine-hydrogen
mixtures is much more complex than in CO + O_2 mixtures, and the results
of the experiments can be only qualitative in nature. With a constant
content of the deficient component, partial replacement of the excess
component by hydrogen fluoride also changes the combustion temperature,
the thermal-conductivity and diffusion coefficients and the average
molecular weight of the mixture. As a result of the large difference
between the molecular weights of the components, combustion of hydrogen-
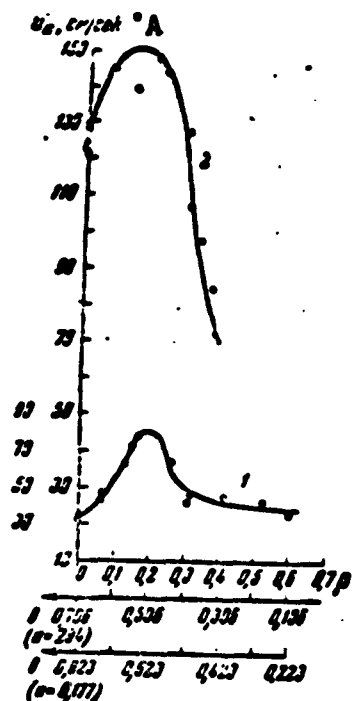chlorine mixtures is accompanied by violation of similarity of the con-

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Fig. 10. Change in normal flame velocity on partial replacement of excess chlorine by hydrogen chloride: 1) $a = 0.177$; 2) $a = 0.294$. A) u_n, cm/sec.
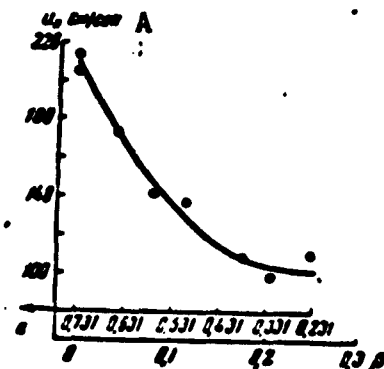
Fig. 11. Change in normal flame speed on partial replacement of excess hydrogen by hydrogen chloride; $b = 0.369$. A) u_n, cm/sec.

centration and temperature fields. For the simplest case, theory enables us to give an approximate evaluation of this factor [15]. However, we can no longer depend on the reliability of such correction with marked dissociation of the combustion products. The lack of additional information concerning the diffusion and thermal-conductivity coefficients and their dependences on composition and temperature renders evaluation of the results obtained even more difficult.

To carry out the experiments, mixtures with equal contents of the deficient component were prepared in two mixers. The excess component of the mixtures to be burned was the second component of each mixture in one mixer, while hydrogen chloride was the excess component in the other. When the two mixtures were combined, the content of the deficient component remained constant, while part of the excess component was

replaced by hydrogen chloride. The mixtures studied were prepared in the explosion flask itself, just as in the experiments with the combustion-product additive.

Mixtures containing 29.4 and 17.7% of deficient hydrogen and 36.9% of deficient chlorine were studied. Figs. 8 and 9 show the combustion temperature and the parameter μ as functions of hydrogen-chloride content for these mixtures. The variations of the normal flame-propagation speeds and replacement of part of the excess component by hydrogen chloride is illustrated by Figs. 10 and 11 ($\underline{a}$ is the mole fraction of hydrogen and $\underline{b}$ is the mole fraction of chlorine).

It should be noted that oxygen additives have little influence on the rate of combustion of chlorine-hydrogen mixtures. It follows from the series of experiments in which part of the excess chlorine was replaced by oxygen that the addition of 10% of oxygen lowers the observed flame speed u_b by 13% (it is necessary to remember that T_b increases somewhat on such a replacement). Hence there is no reason to fear that contamination of the mixtures studied might somehow distort the results of the experiments.

Remarks Concerning the Stability of Normal Combustion in Chlorine-Hydrogen Mixtures

The author also ran several series of experiments in the combustion of chlorine-hydrogen mixtures in a vertical tube open at one end under atmospheric pressure. As we know, the flame front in this case is approximately flat, coinciding with the cross section of the tube, since factors that perturb the flat flame are excluded. This method is applicable for measurements of u_n that do not exceed 0.5 m/sec. At higher values of u_n, the retardation of the combustion products issuing from the tube by friction against the walls results in nonuniform distribution of the gas-flow velocities over the section of the tube, and this

nonuniformity causes distortion of the flame front and accelerates combustion.

The experiments were conducted with tubes 3.5 cm in diameter and 1.1 m long. The tube was capped with a ground-joint head and stopcock through which it was evacuated and the gases admitted. The head was removed directly prior to ignition.

Combustion of mixtures with a chlorine excess indicates that their flame-propagation velocities in tubes are considerably higher than the normal velocities found by the author. Thus, combustion of a mixture with $\gamma = 0.594$ was, to judge from superficial criteria, of the nature of a detonation: observed visually, it appeared to be instantaneous, the tube was shattered by the explosion, which was accompanied by a loud report. At the same time, the normal velocity of the spherical flame in this mixture was only 1.7 m/sec (see Fig. 6). Combustion of a mixture containing 69.4% of Cl_2 with $u_n = 1.1$ m/sec (for a spherical flame) proceeds in a time of the order of 0.1 sec in a similar tube; thus, the flame propagates with an average velocity as high as 10 m/sec, with this velocity even higher in the terminal segment of its path (after the initial acceleration).

This anomalous character of the combustion can be accounted for by the specific properties of mixtures with excess chlorine, in which the diffusion coefficient considerably exceeds the thermal diffusivity; here, similitude of the concentration and temperature fields is essentially violated. Thus, we know from the studies of Ya.B. Zel'dovich and his colleagues [14, 16, 17] that a flat flame may become unstable under such conditions and decompose spontaneously into separate balls and bells.

It may be assumed that a similar phenomenon also occurs in our case. Here, since the normal flame speeds of chlorine-hydrogen mixtures

are quite considerable, spontaneous dismemberment of the front gives rise to its progressive acceleration and turbulization of the combustion, which lead to the appearance of a detonation by the usual mechanism. This mechanism of chemoturbulization and hydrodynamic autoturbulization of normal combustion [18, 19] may be superimposed, amplifying one another.

It remains unclear why this instability is observed only in combustion in tubes and not for spherical flames. We have as yet no answer to this question, and we need only state that the spherical flame is more easily stabilized than a flat flame in the case of internal instability of the combustion mechanism. Thus, instability resulting from violation of similarity of the concentration and temperature fields was observed only for combustion in tubes and not for spherical flames. We note further the effect of the cellular structure of the flame on propagation of slow flames in wide vertical tubes [20] for mixtures with diffusion coefficients both larger and smaller than their thermal diffusivities. In both of these experiments, the Re did not exceed a few hundred, and the spherical flames showed no signs of instability under similar conditions. It would be interesting to make a detailed study of the structure and mechanism by which combustion instability arises in chlorine-hydrogen mixtures by photographing these flames in tubes by both direct and transmitted light.

CONCLUSIONS

1. The propagation of a spherical flame through chlorine-hydrogen mixtures in a glass flask at pressures from 35 to 260 mm Hg was studied.

2. Thermodynamic calculations are presented for the combustion temperature and the density change on combustion of chlorine-hydrogen mixtures as functions of the chlorine-to-hydrogen proportions, the pressure, the amount of combustion products added and the variation

of the content of the mixture's excess component.

3. The normal speed of the flame in chlorine-hydrogen mixtures (except the mixture with $\gamma = 0.823$) does not depend on pressure. The maximum value $u_n = 2.0$ m/sec is attained in binary mixtures of $H_2 + Cl_2$ near the stoichiometric composition.

4. The apparent energy of activation of the reaction in the flame, which was measured for four mixtures, has a constant value of about 34 kcal/mole in chlorine-rich mixtures, drops to 20 kcal/mole for the stoichiometric mixture, and increases to 60 kcal/mole in a mixture with 39.6% Cl_2.

5. The normal speed of the flame was studied as a function of excess-component concentration when part of the excess component was replaced by hydrogen chloride for three series of mixtures.

6. Preliminary experiments in the combustion of chlorine-hydrogen mixtures in tubes justified the assumption that a flat flame in a tube is turbulized more easily than a spherical flame in the presence of internal instability of normal combustion.

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Manu-script Page No.	[List of Transliterated Symbols]
9	Б = B = Bartholome
9	Р = R = Rozlovskiy

IV. KINETICS AND MECHANISM OF REACTION IN FLAME

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CALCULATION OF TRUE TEMPERATURE AND BARIC COEFFICIENTS OF REACTION RATE IN FLAME

The nondependence of normal flame speed on pressure in the simplest version of normal-combustion theory is regarded as an indication of a second order of the reaction in the flame. Here, however, we do not take into account the influence of pressure variation on the combustion temperature of the dissociated reaction products. Let us introduce the appropriate correction, using the method employed for mixtures of $NO + H_2$ [1].

The over-all order $\underline{s}$ of the flame reaction is determined by the expression *

$$s = 2\left[\left(\frac{\partial \ln u_n}{\partial \ln p}\right)_{T_b\,-\,const} + \tfrac{1}{2}\right].$$ (1)

The derivative in the parentheses is computed from the condition

$$\left(\frac{\partial \ln u_n}{\partial \ln p}\right)_{T_b\,-\,const} = \frac{d \ln u_n}{d \ln p} - \left(\frac{\partial \ln u_n}{\partial \ln p}\right)'.$$ (2)

The first term in the right-hand member of (2) is found from experiment; the second term, which characterizes only that part of the baric flame-speed coefficient that is governed by the change in combustion temperature, is determined with the aid of the equation

$$\left(\frac{\partial \ln u_n}{\partial \ln p}\right)' = \frac{d \lg u_n}{d\,(1/T_b)}\,\frac{d\,(1/T_b)}{d \lg p}.$$ (3)

The first derivative in the right member of (3) was determined experimentally; its values were given in the preceding article. The second

cofactor may be computed from the thermodynamic data represented in Fig. 1; its average values for the pressure ranges investigated are presented below:

γ	0.500	0.600	0.700	0.800	0.823
$-d(10^4/T_b)/d\lg p$	2.16	4.20	5.47	3.07	2.05

Let us assume for all four investigated mixtures with $\gamma \geq 0.720$, $d \log u_n/d(1/T_b) = -3.50 \cdot 10^3$ (the value for a mixture with $\gamma = 0.720$ at $p = 0.2$ atm abs), since the temperature coefficient is practically constant in this region; let us further set $d \ln u_n/d \ln p = -0.207$ for $\gamma = 0.823$. Interpolating the values $d(1/T_b)/d \ln p$ on the basis of the data given above, we find, applying Equations (1)–(3):

γ	0.500	0.720	0.762	0.797	0.823
$(\partial \ln u_n/\partial \ln p)_\gamma$	0.0484	0.188	0.105	0.112	0.0714
n	1.90	1.62	1.67	1.77	1.44

Thus, the order of the reaction is found to be near one-and-one-half in chlorine-hydrogen mixtures with weakly dissociated combustion products, in accordance with the reaction mechanism considered in [3] and the laws governing pre-flame kinetics.

Let us compute the true effective activation-energy values in the flame. It was noted in [4] that failure to take into account the temperature dependence of the preexponential multiplier in the equation for flame velocity may result in considerable distortion of the effective activation-energy value. Let us introduce the corresponding improvements into our calculations, assuming that the reaction is of the first order with respect to hydrogen and of order one-and-one-half with respect to chlorine.

The refined equation for the combustion rate takes the form [5, 4]:

$$u_p = \sqrt{\frac{2n_1 l \lambda_m \, \theta^{n+1} \Theta_m}{a_1 c_m \, (T_b - T_0)^{n+1} \rho^2}}. \tag{4}$$

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Here, λ is the thermal conductivity, $\underline{c}$ is the heat capacity of the gaseous mixture, Φ is the reaction rate in the flame, $\underline{a}$ is the dimensionless concentration (grams of component per gram of mixture), $\theta = RT_b^2/A$ is the characteristic temperature interval, $\mathcal{E} = Dc\rho/\lambda$ is the ratio of the diffusion coefficient to the thermal diffusivity, the subscript 1 refers to the deficient component of the mixture, the subscript 2 to the excess component, 0 to the initial ratio, λ_m, $c_m = \lambda$, c $(T = T_b, a_1 = 0)$; $\Phi_m = \Phi (T = T_b, a_1 = a_{01})$; $F = [1 - (z_1/z_2)]^{s_2}$, where $\underline{z}$ is the mole fraction of the corresponding component.

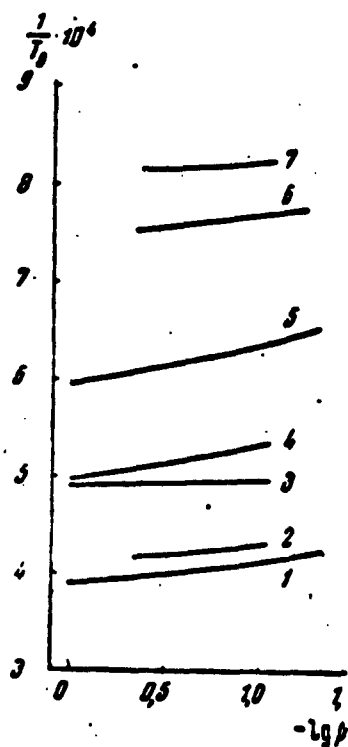Fig. 1. Illustrating determination of true baric rate coefficient of flame in mixtures of $H_2 + Cl_2$: 1) $\gamma = 0.5$; 2) $\gamma = 0.4$; 3) $\gamma = 0.3$; 4) $\gamma = 0.6$; 5) $\gamma = 0.7$; 6) $\gamma = 0.8$; 7) $\gamma = 0.823$.

In mixtures of $H_2 + Cl_2$ in which a fraction α is replaced by combustion products, we have with $\gamma > 0.5$ (excess of chlorine), $s_1 = 1$ and $s_2 = 0.5$,

$$F = \sqrt{1 - \frac{1-\gamma}{\gamma + \frac{\alpha}{1-\alpha}(2\gamma - 1)}};\qquad (5)$$

for $\gamma < 0.5$ $s_1 = 0.5$, $s_2 = 1$,

$$F = 1 - \frac{\gamma}{(1-\gamma) + \frac{\alpha}{1-\alpha}(1-2\gamma)}.\qquad (6)$$

Letting a_{01}^0 and a_{01} denote the initial concentrations before and after dilution with the combustion products, respectively, we write

$$a_{01} = a_{01}^0(1 - \alpha).\qquad (7)$$

Taking into account the dependence of the effective component-concentration values on the combustion temperature and the dilution of the mixture, we set

$$\Phi_m \sim a_{01}^{\nu_1} a_{02}^{\nu_2}\left(\frac{1}{T_b}\right)^{\nu_1+\nu_2} e^{-A/RT_b} \sim \left(\frac{1-\alpha}{T_b}\right)^{\nu_1+\nu_2} e^{-A/RT_b}.\qquad (8)$$
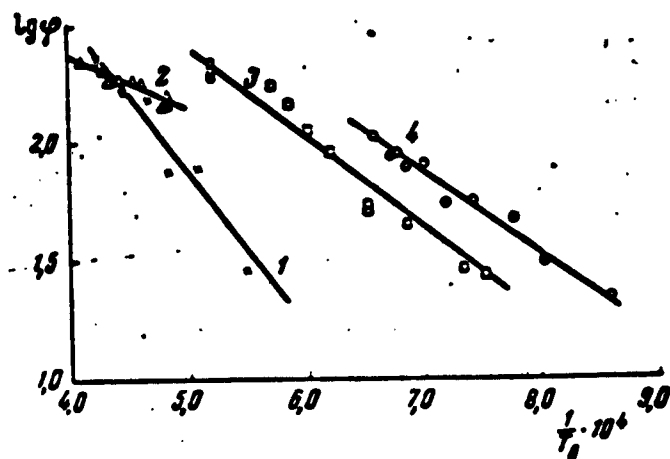
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Fig. 2. Determination of true temperature coefficient of flame velocity in $H_2 + Cl_2$ mixtures: 1) $\gamma = 0.396$; 2) $\gamma = 0.500$; 3) $\gamma = 0.598$; 4) $\gamma = 0.720$.

Since it is assumed that

$$c_m (T_b - T_o) = a_{01} h,$$

(9)

where h is the heat effect of the reaction per gram of deficient component,

$$a_o c_m (T_b - T_o) = (a_{01}^o)^2 h (1 - a)^2.$$

(10)

The quantity λ_m depends only on the combustion temperature, since the composition of the reaction products does not change on dilution. It may be assumed that $\lambda_m \sim (T_b)^{1/2}$, since the Sutherland constant is much smaller than the combustion temperature. Just as in [1], we assume that the parameter ϑ does not depend on temperature and pressure and remains unchanged for experimental series with constant a_{01}^o.

Applying the expressions obtained, we find from Equation (4)

$$e^{-A/RT_b} = \text{const} \frac{u_n^2 (1 - a)^{2 - v - \vartheta_0}(T_b - T_o)^{\vartheta_0}}{f T_b^{2.5 + \vartheta_0 - a_0}} = \text{const } \varphi.$$

(11)

The quantity d log φ/d($1/T_b$), which may be computed on the basis

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of study of the dependence u_n (α) and the results of the thermodynamic calculations, should define the true effective activation energy of the reaction in the flame. Figure 2 presents the results of the experiments described above.

It will be seen from the curves of Fig. 2 that, as for the approximate dependence $\log u_n - (1/T_b)$, the experimental points describing the combustion of all the mixtures investigated show satisfactory fit to straight lines from whose slopes we may compute the following values of A:

γ	0.396	0.500	0.598	0.720
^1A, kcal/mole	66.7	15.1	24.3	22.0

1) A, kcal/mole.

It follows from comparison of the data of the present paper and the preceding one [2] that the values of A' and A of chlorine-hydrogen mixtures differ little from one another. A has the same value — close to that found for the pre-flame reaction [3] — for both of the investigated mixtures with an excess of chlorine.

ANALYSIS OF THE INFLUENCE OF PARTIAL SUBSTITUTION OF THE EXCESS COMPONENT BY HYDROGEN CHLORIDE ON THE KINETICS OF THE REACTION

The complexity of the kinetic relationships in these series of experiments made it impossible to interpret them exhaustively. The speed of the flame must be converted to a standard combustion temperature T_b^0 corresponding (as regards the content of the deficient component) to the basic binary $H_2 + Cl_2$ mixture. A similar subscript will denote the other quantities corresponding to $\beta = 0$. In computing $u_n' = u_n$ (T_b^0) by the equation

$$u_n' = u_n \cdot 10^{B'\left(\frac{1}{T_b^0} - \frac{1}{T_b}\right)}.$$ (12)

where $B' = d \log u_n/d$ $(1/T_b)$, it is necessary to adopt the values of B' found earlier by experiment, i.e., $-3.50 \cdot 10^4$ degrees for a = 0.294

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and 0.177 and $-6.60 \cdot 10^4$ degrees for b = 0.369.

Apart from the combustion temperature, substitution of the excess component by hydrogen chloride also changes thermal conductivity, the average molecular weight of the mixture, and the parameter F. Disregarding the influence of combustion-product dissociation and assuming logarithmic dependence on composition for the average thermal conductivity of the mixture,

$$lg \lambda_m = \sum z_i lg \lambda_i, \tag{13}$$

we find

$$\lambda_m / \lambda_m^o = (\lambda_{HCl} / \lambda_{Cl_2})^\beta \text{ for } \gamma > 0.5, \tag{14}$$

$$\lambda_m / \lambda_m^o = (\lambda_{HCl} / \lambda_{H_2})^\beta \text{ for } \gamma < 0.5. \tag{15}$$

Since

$$\rho / \rho^o = \overline{M} / \overline{M}^o; \quad c_m = C_0 / \overline{M}, \tag{16}$$

where M is the average molecular weight of the mixture and C_0 is its average molar heat capacity,

$$\frac{\mu^o}{\mu} = \frac{\lambda_m \, c_m^o \, \rho^o}{\lambda_m^o \, c_m \, \rho} = \left(\frac{\lambda_{HCl}}{\lambda_{Cl_2} \text{ or } H_2} \right)^\beta \frac{C_0^o}{C_0}. \tag{17}$$

Proceeding from the relationships obtained, we find from (4)

$$\kappa = \frac{u_i'}{u_i^o} = \sqrt{\left(\frac{C_0^o}{C_0}\right)^{n+\gamma\lambda} \left(\frac{\overline{M}^o}{\overline{M}}\right)^{n+\gamma\mu} \left(\frac{\lambda_{HCl}}{\lambda_{Cl_2} \text{ or } H_2}\right)^{\beta(n+\gamma\lambda)} F^2 \left(\frac{x_1}{x_1^o}\right)^a}. \tag{18}$$

In using (18), we bear in mind that with $\gamma > 0.5$

$$F = \sqrt{1 - \frac{x_1}{1 - x_1 - \beta}}, \tag{19}$$

$$\frac{C_0}{C_0^o} = 1 - \beta \frac{C_{Cl_2} - C_{HCl}}{C_0^o}, \tag{20}$$

$$\frac{\overline{M}}{\overline{M}^o} = 1 - \beta \frac{M_{Cl_2} - M_{HCl}}{\overline{M}^o}; \tag{21}$$

for $\gamma < 0.5$,

$$F = 1 - \frac{s_1}{1 - s_1 - s}; \qquad (22)$$

$$\frac{C_0}{C_0^0} = 1 + \beta \frac{C_{HCl} - C_{H_2}}{C_0^0}; \qquad (23)$$

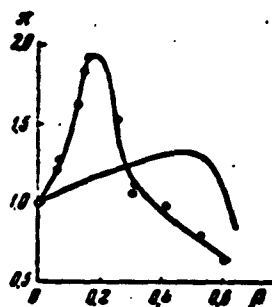$$\frac{M}{M_0} = 1 - \beta \frac{M_{HCl} - M_{H_2}}{M_0}; \qquad (24)$$

Fig. 3. Influence of partial substitution of excess chlorine by hydrogen chloride on speed of flame for mixture with a = = 0.177.
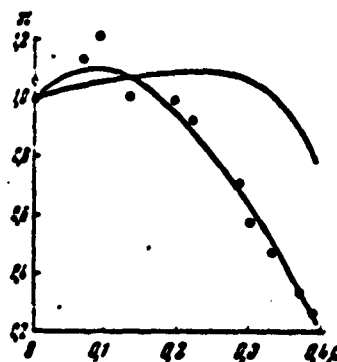

Fig. 4. Influence of partial substitution of excess chlorine by hydrogen chloride on speed of flame for mixture with a = 0.294.
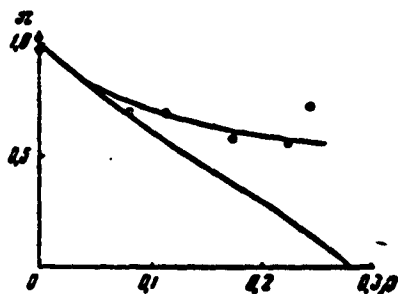

Fig. 5. Influence of partial substitution of excess hydrogen by hydrogen chloride on speed of flame for mixtures with b = 0.369.

It is obvious that the quantities s_1 and s_2 cannot be determined separately in the experimental series under consideration. Further, there is no need to count on high accuracy in the calculations. In addition to the usual approximations of normal-combustion theory, which are aggravated by the inequality of D and $\lambda/c\rho$, we may also have errors stemming from allowance for diffusion of some of the initial components, but not that of the active centers, from the simplified calculation of the ratio v^0/v, and from the unreliability of the

λ_m-values. For the latter, on the basis of the data given by A.M. Markevich [6], we assume

$$(\lambda_{HCl}/\lambda_{Cl_2})_m = 1.94; \qquad (\lambda_{HCl}/\lambda_{H_2})_m = 0.12.$$

Figures 3, 4 and 5 show the experimental and calculated values of π as functions of the hydrogen-chloride content, which have only approximately similar shapes for all three series of experiments. The results of the experiments described confirm the absence of any specific influence exerted on the reaction by hydrogen chloride, which is indeed an inert diluent outside the high-temperature region of profound dissociation.

Since the quantity π depends only slightly on β in all three series of experiments, with the exception of those involving the mixtures closest to stoichiometric, we have no way of drawing more definite or far-reaching conclusions from the results of the measurements considered. The dependence of u_n on the excess-component content, which was to be studied, is masked by a number of side relationships, primarily the influence of inconstancy of the combustion temperature. On introduction of the appropriate corrections, the weak basic dependence that we wish to study is complicated by the influence of the inevitable errors of the corrections introduced; this prevents derivation of quantative conclusions concerning the order of the reaction with respect to each of the components individually.

ABSOLUTE VALUES OF REACTION RATE IN FLAME

The qualitative relationships obtained in the preceding sections permit us the assumption that the reaction kinetics in the flames of chlorine-hydrogen mixtures with chlorine excesses remain the same as in the pre-flame region. Proceeding from this, let us make a comparison between calculated and experimental absolute values of the flame rate

at a standard pressure of 0.2 atm abs for the binary mixtures consider-
ed earlier.

It should be taken into account that the quantity λ_m in the numer-
ator of the right member of (4) is taken for the combustion products at
$T = T_b$. On the other hand, to the extent that we consider the ratio ϑ
to be temperature-independent, while the value of D can be evaluated
only for room temperature, we shall refer the quantity λ that appears
in the expression for ϑ to 273° K and a similar composition.

For mixtures with $\gamma > 0.5$, $s_1 = 1$ and Equation (4) assumes the
form:

$$u_m = \frac{1}{\rho_0} \sqrt{\frac{2F\lambda_m\vartheta^2\Phi_m}{c_{bl}c_m(T_b-T_0)^2\vartheta}} = \frac{RT_b}{p} \sqrt{\frac{2F\lambda_m\vartheta^2\Phi_m}{(1-\gamma)^2 M_{H_2}Q(T_b-T_0)\vartheta}}, \quad (25)$$

where $Q = 44.12$ kcal/mole is the heat effect of the reaction per mole
of deficient component.

In accordance with the relationships established in [3], we may
assume that

$$\Phi_m = 2k_w(T_b) M_{H_2} \sqrt{N_0}(1-\gamma)\sqrt{\gamma}\left(\frac{p}{RT_b}\right)^{n_b}, \quad (26)$$

where k_w is the effective rate constant of the reaction and N_0 is
Avogadro's number. The value of k_w found in [3] from the mechanism of
the pre-flame reaction should be improved by allowing for the probabi-
lity factor of the elementary reaction $Cl + H_2$, $j = 0.18$ [7]. Then

$$k_w = 5.8 \sqrt{T_b} e^{-5400/RT} \text{cm}^{3/2} \text{sec}^{-1}. \quad (27)$$

Then we write

$$\vartheta = \frac{D[2(1-\gamma)C_{HCl}+(2\gamma-1)C_{Cl_2}]}{\lambda_m R \cdot 273}, \quad (28)$$

bearing in mind that the values of C and D are taken for 273° K and
$p = 1$ atm abs.

Substituting the values of Φ_m and ϑ in (25) and remembering that

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$$r = \sqrt{1 - \frac{1 - \gamma}{\gamma}}.$$

we find

$$u_n = \sqrt{\frac{4\sqrt{2\gamma - 1}\, 0^3 k_w (T_b)\, T_b^{2/3} \lambda_m \lambda_{273}}{(1 - \gamma)[2(1 - \gamma) C_{HCl} - (2\gamma - 1) C_{Cl_2}](T_b - T_0) QD} \left(\frac{N_a R^0}{p T_0^2}\right)^{1/2}}. \qquad (29)$$

On the basis of the Sutherland equation, we assume

$$\lambda_m \approx \lambda_{273} \frac{273 + B}{273^{3/2}} \sqrt{T_b}, \qquad (30)$$

where B is Sutherland's constant.

Taking (13) into account, we set

$$\lambda = \lambda_{HCl}^{2(1-\gamma)} \lambda_{Cl_2}^{2\gamma - 1}. \qquad (31)$$

From this, we obtain a final expression for the absolute value of the flame speed in mixtures with $\gamma > 0.5$:

$$u_n = \sqrt{\frac{4\sqrt{2\gamma - 1}\, \lambda_{HCl}^{2(1-\gamma)} \lambda_{Cl_2}^{2\gamma-1} \cdot 0^3 k_w (T_b)\, T_b^2 (273 + B)}{(1 - \gamma)[2(1 - \gamma) C_{HCl} + (2\gamma - 1) C_{Cl_2}](T_b - T_0) T_b QD} \left(\frac{N_a R^0}{p \cdot 273}\right)^{1/2}}. \qquad (32)$$

According to the data presented by A.M. Markevich, at 273° K $\lambda_{HCl} = 3.52 \cdot 10^{-5}$ and $\lambda_{Cl_2} = 1.83 \cdot 10^{-5}$ cal/cm-sec-degree. Further, we set $D = 0.50$ cm^2/sec, $C_{HCl} = 6.95$, $C_{Cl_2} = 8.08$ cal/mole-degreee and $B = 240$. Substituting the values of the physicochemical constants in (32) and remembering that $p = 0.2$ atm abs, we find

$$u_n = 4.92 \sqrt{\frac{\sqrt{2\gamma - 1}\, T_b^{2.6}}{(1 - \gamma)(2.575 + \gamma) \cdot 10^{1.12\gamma + 7.6T_0/T_b}\, T_b\, (T_b - 273)}}. \qquad (33)$$

The results of the calculations are presented in Fig. 6 of Reference [2] (curve A). As will be seen from the figure, the results of experiment and calculation are in practical agreement, and the error of the calculations is (by coincidence) even smaller than the possible error for the existing inexactness of the theory and our information concerning the physicochemical properties of the reaction components.

Marked divergences begin to appear around the stoichiometric composition, where our conception ceases to be valid. The agreement between the calculated and experimental values of u_n is due to the simplicity of the mechanism and the stability of the reaction kinetics of the chlorine-hydrogen mixture. These conditions made possible extensive extrapolation of the kinetic characteristics, and the rate constants of the reaction in particular, from the investigated region of temperatures of the order of $500-600^{\circ}$ K to the combustion temperature.

Formally, extension of the calculation results for the absolute values of u_n to the region of mixtures with excess hydrogen is not expedient. The combustion of these mixtures apparently has an essentially different mechanism, and it cannot be described by mechanical application of a kinetic equation based on a conception of equilibrium dissociation of chlorine in the reaction zone.

REACTION MECHANISM IN FLAME AND CONDITIONS FOR GENERATION OF ACTIVE CENTERS

The results of measurement of the baric and temperature coefficients of flame speed affirm the hypothesis that the reaction in the flames of mixtures with excess chlorine proceeds by the same mechanism as in the pre-flame region. In these flames, there is time for establishment of equilibrium dissociation of the chlorine.

The magnitude of the activation energy for a mixture with excess hydrogen suggests that the formation of chlorine atoms is effected here by another mechanism; here, its value corresponds to nonequilibrium dissociation of the chlorine taking place on double collisions with energies equal to ≥ 57 kcal/mole, which split the chlorine molecule. The theoretical value of $A = 63$ kcal/mole, which is formed from the sum of the dissociation energy of chlorine and the activation energy of the slow elementary reaction between $Cl + H_2$, 6 kcal/mole, is close to the

experimental value of 66.7 kcal/mole.

It must be remembered that the formation of atomic chlorine on combustion of mixtures with $\gamma > 0.5$ is possible in any region of the flame where the temperature is high enough, including in the combustion products themselves, with subsequent diffusive transfer of active centers into the reaction zone. In the presence of a hydrogen excess, however, chlorine atoms can form only in a narrow region, since the concentrations of atomic and molecular chlorine in the zone where the temperature approaches T_b are practically zero, while at low temperatures the number of active collisions is still small. For this reason, equilibrium dissociation of chlorine is naturally rendered more difficult in mixtures with excess hydrogen.

The most difficult part of the problem of the reaction mechanism in the flame consists in determining the way in which equilibrium dissociation of the chlorine occurs. As we know, analysis of macrokinetic relationships in any chain reaction normally does not make possible direct determination of its mechanism and results in the construction of hypothetical, ambiguous reaction schemes. To offset this, however, the extreme simplicity of the H — Cl system and the thoroughness with which the kinetics of its elementary stages has been studied reduce the number of possible assumptions as to the reaction mechanism to a minimum and facilitate their verification.

In view of the high temperature in the reaction zone, we can no longer unconditionally exclude dissociation of the chlorine on double collisions $M + Cl_2$, as was done for the low-temperature process. However, this solution of the problem will not be adequate, since, on the basis of analysis of self-ignition conditions [7], it is obviously necessary that some chain-branching mechanism exist at moderate temperatures to provide for a progressive increase in the active-center con-

centration in the isothermal regime. These branching events will take place as the reaction proceeds in the flame.

The following hypotheses have been advanced concerning the possible branching mechanisms.

1. Dissociation of chlorine in the cold chlorine-hydrogen mixture under the influence of radiation from layers burned previously.

2. Dissociation of chlorine in triple collisions:

$$H + 2Cl_2 = HCl + 3Cl - 12.6 \quad \text{kcal/mole (at } 1600^{\circ}K). \tag{T}$$

It may be assumed that the probability of this process is relatively high due to the high exothermic heat effect of the H + Cl_2 reaction (46.6 kcal/mole at 1600° K).

3. Dissociation of the chlorine on collisions with the excited HCl * molecules formed in the exothermic reaction of H + Cl_2:

$$H + Cl_2 = HCl^* + Cl; \quad HCl^* + Cl_2 = HCl + 2Cl \tag{E}$$
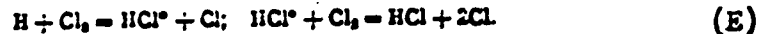
The autophotochemical mechanism [scheme (1)] is rather improbable because the elementary emission event cannot transfer an energy larger than that liberated in the exothermic stage H + Cl_2, and this quantity is inadequate to dissociate chlorine at room temperature. Further, if dissipation of the energy of the excited chlorine molecules after absorption takes place during a time that is short as compared with the flame-propagation time, it is most probable that absorption of light is equivalent to a certain increase in the mixture's thermal conductivity. It is obvious that the latter will not introduce any marked distortions, as is attested to by the agreement between the experimental and calculated values of u_n. If, on the other hand, dissipation of the energy takes place slowly, the speed of the flame cannot remain constant over its path because of the nonsteady light-absorption conditions, and this

is not the case.

It will subsequently be necessary to take into account the remark of Rice [8] to the effect that in the dissociation of bromine and iodine, the preexponential factor of the rate constant of the reaction $M + Hal_2$ exceeds that computed by the formula of the kinetic theory of gases (for effective cross sections found from the viscosity of the gases) by a factor of 100. This departure is due to the considerable energy difference between the halogen molecules in the state preceding dissociation and the same molecules in the normal state. To estimate the magnitude of the rate constant of the reaction $M + Cl_2 \overset{k_d}{\rightleftharpoons} M + 2Cl$, we shall employ the data of Rabinowitch and Wood [9, 10] on the kinetics of recombination of atomic bromine and iodine on triple collisions with various gases (M), determining the corresponding value of the recombination constant k_a for chlorine by extrapolation.

Since we are interested in mixtures with excess chlorine, the properties of the recombining third particle M must be averaged between the properties of HCl and Cl [$\sqrt{k_a \text{ (HCl)} \ k_a \text{ (Cl}_2\text{)}}$].

In the case of recombination of bromine, $k_a \cdot 10^{32} \approx 20$ cm^6/sec for $M = Br_2$ and 3.2 for $M = O_2$ (the latter is closest as regards physical properties to HCl among the gases studied). On the basis of Rabinowitch and Wood data, we may consider k_a (Br)/k_a (I) ≈ 0.30. Assuming that the ratio k_a (Cl)/k_a (Br) has the same value, we find for the recombination $Cl + Cl + M$, $k_a \cdot 10^{32} = 2.4$ cm^6/sec.

We find the value of k_d from the relationship k_d (Cl)/k_a (Cl) $= K_{Cl_2}$, where $K_{Cl_2} = \sqrt{n_{Cl_2}}$ is the dissociation constant of chlorine. Since $K_{Cl_2} = ge^{-L/2RT}$, where L = 56.9 kcal/mole is the heat of dissociation of chlorine, $g = 2.1 \cdot 10^{12}$ cm$^{-3/2}$, and the activation energy of recombination is usually considered to be zero, $k_d(Cl) = 1.1 \cdot 10^7 e^{-L/2RT}$

[cm^3/sec]. Comparing this value with that computed from the number of M + Cl$_2$ collisions (M = HCl + Cl$_2$) at 1600° K, we find that the rate constant of the dissociation of chlorine exceeds that calculated from elementary theory by a factor of ω = 230.

The mechanism of "energy" branching is similar to the mechanism of positive chain interaction proposed (during development of the chain theory) by N.N. Semenov [11], with the difference that it does not require simultaneous participation of two excited HCl* molecules (HCl* + + HCl* + Cl$_2$ = 2HCl + 2Cl), which, as was established in subsequent studies of Semenov's school, can hardly be realized. At the same time, this mechanism also resembles that of trimolecular branching 2, the only essential difference being that one triple collision is replaced by two successive double collisions. "Energy" branching may take place given adequate lifetime of the excited molecule HCl*: if the latter is commensurate with the time between collisions of the molecules of the mixture under consideration.

For the time being, we shall not attempt to give a rigorous quantative basis for the possibility of equilibrium dissociation of chlorine in the flame, but only attempt a selection among the alternative mechanisms of trimolecular and "energy" branchings. If progress of the trimolecular branching reaction (T) requires an activation energy A_T, the lower-limit value of which should be regarded as 12.6 kcal/mole, the rate of formation of atomic chlorine by this mechanism is

$$(dn_{Cl}/dt)_T = 3k_T n_H n_{Cl_2}^2 e^{-A_T/RT},\qquad(34)$$

where k_T is the constant of the triple collisions H + Cl$_2$ + Cl$_2$, incorporating a factor similar to ω. Accordingly, we find for the "energy" mechanism

$$(dn_{Cl}/dt)_E = 3\, k_E n_{HCl} \cdot n_{Cl_2} e^{-A_E'/RT}.\qquad(35)$$

where k_E is the constant of the double collisions HCl* + Cl₂.

It might be assumed that $A_r = A'_r$, since the energy relationships remain unchanged if the reaction H + 2Cl₂ is broken down into two stages. Since the HCl* is deactivated primarily by collisions and not by spontaneous emission, we have in the quasistationary state

$$dn_{HCl*}/dt = k_2 n_H n_{Cl_2} - \varepsilon k^* n_{HCl*} n_M = 0. \qquad (36)$$

Here, k_2 is the known [7] rate constant of the H + Cl₂ reaction, k* is the constant of the double collisions HCl* + M, and ε is the deactivation probability of HCl* on collisions; we shall henceforth set $\varepsilon = 1$, which will give the lower limit of the rate of formation of atomic chlorine by the "energy"-branching mechanism. Equations (35) and (36) give

$$\left(\frac{dn_{Cl}}{dt}\right)_E = 3\left(\frac{k_E k_2}{k^*}\right) n_H \left(\frac{n^0_{Cl_2}}{n_M}\right) e^{-A_p/RT}. \qquad (37)$$

$$\frac{(dn_{Cl}/dt)_E}{(dn_{Cl}/dt)_T} = \frac{k_E k_2}{k^* k_1 n_M}. \qquad (38)$$

Due to the excited state of the HCl* molecule, the factor ω in the expression for k_E must be larger than for k_T, but a similar correction must be introduced and the expression [sic; into the expression] for k*, which also characterizes the HCl* collisions. Taking these circumstances into account and applying the formulas of the kinetic theory of gases, we find

$$\frac{k_E k_2}{k^* k_T n_M} = \frac{j e^{-\Delta\omega/RT}}{4\pi\sigma^2_{Cl_2} n_M}. \qquad (39)$$

where $j = 0.18$ is the probability factor of the reaction H + Cl₂, σ is the effective cross section. It follows from (39) that with the assumption $\varepsilon = 1$ that we have made, which lowers the rate of the "energy"-branching reaction, this rate for the experiments described is two orders of magnitude larger than for trimolecular branchings.

It should be noted that the mechanism of "energy" branching does not in any way contradict prevailing conceptions of the impossibility of "energy" chains with excited molecules as their basic links. The formation of chemically active radicals is always an unconditionally more favorable path for the development of the reaction in view of the short lifetime of the excited molecule. In this case, however, the extreme simplicity of the system does not leave open any other possibility for branching except for transfer of the energy of the excited product of the exothermic reaction $H + Cl_2$ by elementary event. In the light of the above, "energy" branchings are an exception that tends to prove the basic rule.

The above considerations as to the nature of "energy" branching may not be regarded as exhaustive; nevertheless, they are adequate as a working hypothesis to account for this new interesting type of chain reaction. At the same time, the basic kinetic relationships of the dark reaction in the chlorine-hydrogen mixture may be regarded as established, together with their maximum stability over a wide temperature interval; the qualitative relationships found confirm the applicability of methods of normal-combustion theory to the problems of chemical kinetics.

CONCLUSIONS

1. The baric rate coefficient of the flame reaction, corrected to allow for the dependence of combustion temperature on pressure, corresponds to a reaction order of one-and-one-half.

2. The corrected temperature coefficient of the reaction rate in the flame in mixtures with excess chlorine corresponds to the true effective activation-energy value, which is close to that found for the pre-flame reaction: 34.7 kcal/mole. In mixtures with excessive hydrogen, the quantity A is close to the sum of the dissociation energy of chlorine and the activation energy of the elementary reaction $Cl + H_2$. In the stoichiometric mixture, the magnitude of the temperature coefficient is distorted by the profound dissociation of the combustion products.

3. The influence of excess-component concentration on the reaction rate in the flame is severely distorted by side factors. The results obtained in an attempt to take these complications into account were only approximately similar to the experimental results.

4. The absolute reaction-rate values in the flames of binary mixtures with chlorine excess agree well with the speeds calculated from the reaction mechanism and from data on the kinetics of the pre-flame reaction, thus confirming the fact of equilibrium dissociation of chlorine in the flame.

5. Homogeneous formation of an equilibrium quantity of atomic chlorine in the flame by the mechanism of radiation from the burning layers and trimolecular branching is doubtful. The probable mechanism of formation of atomic chlorine in the flame is formed by "energy" branchings on collisions between chlorine molecules and excited HCl* molecules formed during the reaction.

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Manu-script Page No.	[Footnote]
20	The symbols are explained in [2].

Manu-script Page No.	[List of Transliterated Symbols]
34	p = r = razvetvleniye = branching

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